

Selective catalytic oxidation of hydrogen sulfide: influence of surface characteristics and sodium hydroxide on the catalytic activity of activated carbons

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Introduction

Sulfur-containing compounds must be removed at the early stage of hydrogen production and purification processes because of their strong poisoning effects on the processing catalysts and PEM fuel cell. Direct oxidation of H₂S to elemental sulfur by the use of a selective catalyst such as activated carbon is believed to be a preferred approach for dilute H₂S-containing gas streams [1]. This technique has the possibility of reducing sulfur to the part-per-billion level and the advantage of being insensitive to steam. One of the major technical challenges associated with achieving selective oxidation of H₂S is the formation of other undesirable sulphur pollutants; namely, sulphur dioxide (SO₂) and carbonyl sulphide (COS) [2,3]. To minimize the formation of these compounds, previous research in our laboratory was focused on optimizing process conditions to achieve a high level of selective oxidation [3]. Our goal in this reported work is to characterize the surface and structural features of various activated carbon materials and correlate these properties with the catalytic activity of the carbon materials. In this context, particular attention was given to the porosity and surface functionality of the activated carbon materials examined. The effect of impregnation with a solution of sodium hydroxide on the catalytic performance of activated carbons was also studied. Commonly, when the process of catalytic oxidation is involved, impregnation of activated carbons with active reagents as, for instance, metal oxides [4], ammonia [5], urea [6], and alkaline materials [5] could improve the catalytic properties of activated carbons. The catalytic performance of impregnated and unimpregnated activated carbons were analyzed in terms of the capacity of carbons for hydrogen sulfide (H₂S) removal from hydrogen-rich fuel streams, and the emission times of H₂S and the products of its oxidation, sulfur dioxide (SO₂) and carbonyl sulfide (COS).

Materials and Methods

Several commercial and lab-made activated carbons were tested in a fix-bed reactor system described elsewhere [3]. Different precursors and activation processes were used to produce carbon catalysts with variable microstructures and impurity levels. Activation was achieved by exposing the carbon precursor to an oxidizing gas, CO₂, for variable lengths of time. Impregnation with NaOH was done by mixing 20ml of carbon with 20 ml of a solution of NaOH of variable concentration for two hours. The samples were dried at 110°C for 24 hours. The weight percent of NaOH in the impregnated activated carbon was calculated as the weight of NaOH divided to the weight of carbon. The selective oxidation reaction was conducted at atmospheric pressure with a space velocity of 3100 h⁻¹ (GHSV) and a total gas flow rate of 0.5 L/min. The catalysts were tested in a stream of pure H₂ and a simulated reformat fuel containing 1000 ppm of H₂S. A typical simulated reformat gas mixture contained 50% H₂, 15% CO₂, 9% CO, 2% N₂, and 24% balance H₂O in volume. Air was introduced into the influent gas stream at the rate necessary to achieve a 2:1 O₂:H₂S ratio.

Results and Discussion

The catalytic behaviour for the selective oxidation of H₂S to sulphur of a series of activated carbons examined was greatly altered due to changes in chemical and structural characteristics. We have found that porosity of the carbon plays a role in controlling the activity and deactivation rate in H₂S oxidation reactions. However, it seems that not only the

presence of micropores is important, but also the presence of interconnecting mesoporous structures. The presence of oxygen-containing groups on the carbon surface did not appear to affect the catalytic activity or selectivity values of the carbons studied. In contrast, a linear correlation was found between the nitrogen content of the carbons and their capacity for H₂S oxidation in hydrogen streams. The correlation in this respect was much less clear for reformat streams. Impregnation of activated carbons with NaOH significantly improved their catalytic performance. As presented in Figure 1 for two selected activated carbons studied (labeled in the figure as WSC and VA), the specific H₂S capacity of the carbons was increased after NaOH impregnation along with the emission times of the sulfur-containing products. The increase in H₂S capacity of the carbons is likely due to a facilitated mechanism of dissociation of H₂S to HS⁻ in the presence of NaOH and its further oxidation.

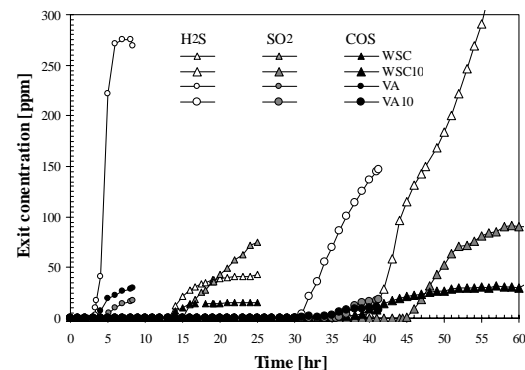


Figure 1: Breakthrough curves in reformat for two of our activated carbons before (WSC and VA) and after (WSC10 and VA10) impregnation with 10% NaOH

Significance

The removal of sulfur from hydrocarbon feedstocks has become crucial for the development of the fuel cell and hydrogen industries. The fundamental understanding of the catalytic properties of activated carbons will enable the tailoring of these catalysts to yield greater sulfur removal efficiency.

References

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This research was sponsored by the U.S. Department of Energy through the Offices of Fossil Energy and of Hydrogen, Fuel Cells and Infrastructure Technologies (under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC, at Oak Ridge National Laboratory (ORNL)). The research was supported in part by an appointment to the ORNL Postdoctoral Research Associates Program administered jointly by the Oak Ridge Institute for Science and Education (ORISE) and ORNL.